

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 7 : C09K 21/02, C08K 3/00</p>		<p>A1</p>	<p>(11) International Publication Number: WO 00/68337 (43) International Publication Date: 16 November 2000 (16.11.00)</p>		
<p>(21) International Application Number: PCT/GB00/01792</p>		<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p>			
<p>(22) International Filing Date: 11 May 2000 (11.05.00)</p>					
<p>(30) Priority Data: 9910774.0 11 May 1999 (11.05.99) GB 0004567.4 28 February 2000 (28.02.00) GB</p>					
<p>(71) Applicant (<i>for all designated States except US</i>): WOLSTEN-HOLME INTERNATIONAL LIMITED [GB/GB]; Lower Eccleshill Road, Darwen, Blackburn, Lancashire BB3 0RP (GB).</p>		<p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>			
<p>(72) Inventor; and</p>					
<p>(75) Inventor/Applicant (<i>for US only</i>): CROMPTON, Geoffrey [GB/GB]; 24 Albert Road, Southport, Merseyside PR9 0LG (GB).</p>					
<p>(74) Agent: ROYSTONS; Tower Building, Water Street, Liverpool L3 1BA, Merseyside (GB).</p>					
<p>(54) Title: FIRE BARRIER MATERIALS</p>					
<p>(57) Abstract</p> <p>A fire barrier material comprising a combination of materials capable of melting progressively as the temperature rises under fire conditions, namely a relatively high melting devitrifying frit, one or more substances to reduce melt and flow temperature of the frit and, optionally, an intumescent substance and/or a pH buffer. The material is particularly suitable for use in thermoplastic materials.</p>					

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

Title: Fire Barrier Materials

DESCRIPTION

This invention concerns fire barrier materials.

Fire barrier materials are known from GB2234754A in the form of compositions comprising two or more frits capable of melting progressively as the temperature rises in a fire situation; one of the frits being a relatively high melting devitrifying frit. The composition can be added to a variety of materials such as phenolic and polyester resins and sodium silicate, to provide or enhance fire resistance.

A preferred composition contains a relatively low melting frit that starts to melt at about 450°C and a devitrifying frit that starts to melt at about 700°C. The devitrifying frit specifically solidifies or vitrifies to provide strength to the char forming a fused protective layer, thus starving the fire of oxygen and reducing smoke and toxic fume emissions as well as reducing the risk of flashover.

It is also known to add to such frit compositions intumescent substances, such as hydrated magnesium hydrated carbonate, calcium carbonate and alumina trihydrate. These intumescent substances give off water vapour and carbon dioxide in a fire situation and together with the frit composition help to stop flaming of the host material. Melamine phosphate as one intumescent additive and a combination of ammonium polyphosphate, melamine and pentaerythritol (trade name "Budit 3077") as another have been included in frit compositions to give an intumescent char in fire situations. Melamine phosphate mixed with a frit composition and a phosphate flame retardant in

powder form has proved effective in both epoxy and polyester resins.

Frit compositions of the type described above are sold under the trade mark CEEPREE and have been used in coatings, paints, sealants, caulk, adhesives, polyester and phenoic dough and sheet compounds, vinyl flooring, EPDM sheet and other materials to provide fire barrier properties.

However, these frit compositions are not entirely suitable for use in certain materials, such as thermoplastics used in injection and extrusion moulding processes for forming end products, such as communications and electric power cables, electrical components, automobile, aircraft, domestic and industrial buildings and marine craft parts, and thermosetting materials and composites, such as glass reinforced resin laminates used for moulding storage tanks and the like.

In particular it has been found that the prior art frit compositions have an alkaline pH of the order of 10 which has precluded their use in some paints and sealants having an acid pH, such as those based on acrylic resins.

It has also been found that the softening temperature of 450°C of a lower melting frit is too high for its use in some host materials, such as thermoplastics, because they degrade at much lower temperatures. The host material could be protected to over 450°C by including alumina trihydrate, hydrated magnesium calcium carbonate or magnesium oxide but the volumes of these materials needed to be effective affects processing and properties of the end product.

An alternative is to use halogenated systems based on chlorinated paraffins or brominated materials with antimony trioxide or pentoxide. However, the use of these systems is being curtailed because of their carcinogenic properties and the increase in smoke production in a fire situation.

An object of this invention is to provide frit compositions having a wider range of

uses than hitherto.

According to a first aspect of this invention there is provided a fire barrier material comprising two or more frits capable of melting progressively as the temperature rises under fire conditions, one of said frits being a relatively low-melting frit and another of said frits being a relatively high melting devitrifying frit and at least one of

- (a) a pH buffer;
- (b) one or more of substances to reduce melt and flow temperature of the frits; and
- (c) an intumescent substance.

According to a second aspect of this invention there is provided a composition of glass frits comprising at least one low melt frit and at least one devitrifying or high temperature melting frit and a powder blend to neutralise pH of the composition and to drop the melt and flow temperature.

According to a third aspect of this invention there is provided a fire barrier material comprising a combination of materials capable of melting progressively as the temperature rises under fire conditions, namely a relatively high melting devitrifying frit, one or more substances to reduce melt and flow temperature of the frit and optionally an intumescent substance.

The material according to the third aspect of the invention may also include a pH buffer.

According to a fourth aspect of the invention there is provided a composition comprising a devitrifying or high melting temperature frit and a powder blend to neutralise pH of the composition and to drop the melt and flow temperature.

The powder blends may be selected from ammonium molybdate, sodium pyrophosphate, ammonium monophosphate, ammonium polyphosphate, zinc borate,

zinc and tin powdered metals, melamine, pentaerythritol and melamine phosphate.

The preferred substance pH buffer is one that reduces the pH of the frit compositions to a low alkalinity or neutral pH. A pH reduction to 8.5 or even 7 is desirable and would render the frit compositions of the invention capable of being used in aqueous acrylic resin based materials.

Compositions of the invention may be used in acid and ester cured thermosetting resins used in glass fibre reinforced structures. They may also be used in catalyst cured thermosetting resins, such as phenolic, epoxy and polyester resins, which would otherwise have the catalyst neutralised by the high pH of the blends.

Suitable pH buffers include phosphates, such as, for example, sodium pyrophosphate, ammonium monophosphate and ammonium polyphosphate.

Another advantage of some of these buffer substances is their ability to generate gases under heat, such as when in combination with zinc borate, the gases causing foaming of the frit composition so that carbonaceous char from the hot material can fill the foam cavities to form a protective skin in a fire situation.

The substances to bring down melt and flow temperatures may be used singly or in combinations. A preferred combination produces a first melt zone in the range of 220 to 270°C, a second melt zone in the range 270 to 420°C and a third melt zone in the range of 420°C upwards.

One substance to bring down the melt and flow temperature of the frit compositions of the invention may be zinc borate. The inclusion of zinc borate which starts to function at 350°C has proved effective in bringing the melt and flow temperature of the frit mix down. Magnesium carbonate and/or zinc spar may be added to the zinc borate to reduce the melt temperature further. When used in conjunction with sodium pyrophosphate and the frit mix, the blend is inert until heated beyond 350°C. At

that point the materials begin to fuse and the gas generated by the action of heat causes an intumescence action in the molten glass compound. A fine celled glass foam is produced without the inclusion of melamine as a blowing agent and pentaerythritol as a carbonific which would be the normal specification to obtain this effect. It will be appreciated that the decreased trigger temperature of 350°C may still not be low enough for the inclusion of frit compositions of the invention in some host materials.

It has been found that the inclusion of some powdered metals in the glass frit mix can bring the melt temperature of the blend down to a viable level, i.e. a temperature which will allow heat operated processes, such as injection moulding and extrusion, to be carried out without triggering the melt and flow characteristics within the equipment, whilst forming a protective char on the surface of the host material in a fire situation.

Powdered tin with a melt temperature of 228°C may be used in a small quantity, as a catalyst, to promote a cascade effect. Powdered zinc with a melting temperature of 420°C may be added as the second metal. Zinc borate may also be included as a third component. Tin, zinc and zinc borate can be mixed in any proportions for use in compositions of the invention. A mix of tin and zinc is the preferred blend for use in compositions of the invention.

There are possible electrical disadvantages when the frit mix fuses in a fire situation, particularly in electrical cable covering material. A covalent bond is the linkage of two atoms by the sharing of two electrons, one contributed by each of the atoms. The electrons are only shared equally when the atoms are identical and in most covalent bonds the electrons are held to a greater extent by one atom than the other, leading to electronegativity. Negative ions can be produced. The inclusion of materials with free positive ions can be of considerable benefit.

Tin is largely covalent in the +2 state. Zinc and zinc borate are in the +2 state, generally in octahedral or tetrahedral co-ordination and readily form complexes. The addition of small quantities of these metals can stabilise the electron balance during the process of fusion.

Zinc forms a bond with some of the components present in the frit mix. Zinc orthosilicate $Zn SiO_4$ forms a glass on heating which cannot have a continuous network of SiO_4 units because each is separated by a zinc atom. The zinc, therefore, takes on a network forming role, thus strengthening the glaze formed as the glass frit composition melts and flows. This contributes to the formation of a vitreous glaze on the surface of the char which stops oxygen ingress and the exit of smoke and toxic fumes. The production of these unburned gasses, which normally escape together and gather below ceiling level, before exploding, can be partially delayed by this glassy char. This means that the phenomenon known as 'flashover' can be minimised in some cases.

It is well known that powdered metals such as tin and zinc burn in air when strongly heated. When included in compositions or blends of the invention containing zinc borate and sodium pyrophosphate there is virtually no trace of this phenomenon. The hydrogen gas generated causes the molten composite to intumesce and form a fine cell glass foam when subjected to fire. This foam has the advantage of housing the carbonaceous char within its cells to give good insulation to the substrate. The hydrogen gas can also coat the surface of the char to act as an electrical insulator.

The char being an amalgam of glass and metal, has an intrinsic strength which can withstand wind and water spray to a much greater extend than the normal intumescent.

A preferred substance for use in compositions of the invention is mica. Mica is an aluminosilicate with layers of linked $(SiAlO_4)$ tetrahedra. Muscovite mica is a

relatively soft mineral with a low co-efficient of expansion. It is electrically insulating, with good thermal stability and chemical resistance. When included with the frit blend, at a suitable particle size it contributes to the overall performance in a fire situation. It starts to evolve water vapour between 500°C and 900°C and it contributes to the flow characteristics by combining with the frit mix at temperatures between 600°C and 800°C. Mica acts as a high temperature adhesive in these conditions, helping to hold the char together and stop cracking as the char cools.

Boric acid may be included in blends and compositions of the invention as a glass forming material at low temperatures. However, its degradation temperature of about 100°C is too low for its inclusion in thermoplastic processing and it is almost totally water soluble. Therefore, before its inclusion in blends and composition of the invention it needs to be coated. A suitable coating material is a silicone oil, such as Dow Corning's silicone oil 1107, which serves to increase the degradation temperature to an acceptable level. Boric acid can be included in blends and compositions of the invention in amounts of from 5 to 100 pph.

The blends and compositions of the invention may be provided in powder form of such particle sizes that when incorporated in plastics materials allow for extrusion without blockage. Furthermore, the powders can be waterproof of sufficiently low degradation temperature to protect thermoplastics mouldings and extrusions without being triggered in the processing.

The composition of the invention can be all coated with a variety of materials which can help in mechanical and electrical properties. Amino silane has proved effective in EVA filled with Ath, stearate coating with polyethylene, polypropylenes, EPDM, and chorosulphonated polyethylene. The preferred coating is silicone orthosilicate 1107 from Dow Corning. This silicone polysiloxane allows the blends of

the invention to be used in any material and gives a waterproof finish. This enables the coated material to be used in catalyst cure resins, such as phenolic, epoxy and polyester resins, without the catalyst being neutralised.

The invention will now be described by means of the following Examples:-

Blends of powders were made up in a variety of compositions. The compositions of Examples 1 to 14 were subjected to the heat of a muffle furnace and a variety of temperatures and time scales. Notes were taken as to the temperature and duration of melt, flow, intumescence, and set characteristics and evaluation of electrical insulation, and levels of smoke and toxicity produced. Two standard frit mixes were used in all experiments. The first has a particle size of 30 micron and the second is at 5 microns. Mixes of the following materials in the ratios of 5 parts per hundred to 95 pph were made and tested in conjunction with each other, and individually as a sole additive, to the common material Ceepree® at 100 pph.

The compositions of Examples 15 to 23 were subjected to the heat of a thermomicroscope from 200°C to 1000°C. Photographs were taken together with data on the temperature and duration of melt, flow, intumescence and set characteristics and evaluation of electrical insulation and levels of smoke and toxicity produced. Mixes of the following materials in the ratios of 5 parts per hundred to 95 pph were made and tested in conjunction with each other, and individually as a sole additive, to the common devitrifying frit at 100 pph.

Example 1	Ceepree® at	30 microns 100 parts
	Tin at	10 pph
	Zinc at	10 pph
	Zinc Borate at	10 pph

Sodium Pyrophosphate at 10 pph

This mix gave a melt and flow temperature of 230°C with an intumescence starting at 450°C and ceasing at 800°C.

Example 2

Ceepree® M at 5 microns 100 parts together with the formula as in Example 1. The results were very similar. The composition was more suitable for extrusion and injection moulding because of the small particle size, although more expensive to produce.

Example 3

As Example 2 but with the addition of 10 pph of fine ground mica. The result was an improved electrical insulation when compounded and extruded both at room temperature and in a simulated fire.

Example 4	Ceepree ® at	30 microns 100 parts
	Tin at	15 pph at 5 micron
	Zinc at	30 pph at 5 micron
	Mica at	30 pph at 5 micron

Example 5	Ceepree ® at	5 microns 100 parts
	Tin at	15 pph at 5 micron
	Zinc at	45 pph at 5 micron
	Mica at	30 pph at 5 micron

10

Example 6	Ceepree ® at	30 microns 100 parts
	Tin at	10 pph
	Bismuth at	5 pph
	Zinc at	20 pph
	Zinc Borate at	10 pph
	Sodium Pyrophosphate at	10 pph
Example 7	Ceepree ® C200 at	30 microns 100 parts
	Tin at	10 pph
	Mica at	10 pph
	Zinc at	10 pph
	Zinc Borate at	10 pph
	Sodium Pyrophosphate at	10 pph

Example 8

Ceepree ® M at 5 microns 100 parts together with the formula as in Example 7. The results were very similar. The composition was more suitable for extrusion and injection moulding because of the small particle size, although more expensive to produce.

Example 9

As Example 8 but with the addition of 10 pph of fine ground ammonium molybdate (AOM). The result was an improved electrical insulation and smoke reduction when compounded and extruded both at room temperature and in a simulated fire.

Example 10	Ceepree ® at	30 microns 100 parts
	Tin at	5 to 15 pph at 5 micron
	Zinc at	5 to 30 pph at 5 micron
	Mica at	5 to 30 pph at 5 micron
	Zinc Borate at	5 to 30 pph at 5 micron
Example 11	Devitrifying frit at	5 microns 100 parts
	Tin at	5 to 15 pph at 5 micron
	Zinc at	5 to 45 pph at 5 micron
	Mica at	5 to 30 pph at 5 micron
	Zinc Borate at	5 to 30 pph at 5 micron
Example 12	Ceepree ® at	30 microns 100 parts
	ammonium molybdate (AOM) at	1 to 5 pph
	Tin at	10 pph
	Zinc at	20 pph
	Zinc Borate at	10 pph
	Sodium Borate at	10 pph
	Sodium Pyrophosphate at	10 pph
Example 13	Devitrifying frit at	5 microns 100 parts
	Tin at	5 to 15 pph at 5 micron
	Zinc at	5 to 45 pph at 5 micron
	Mica at	5 to 30 pph at 5 micron

12

Zinc Borate at	5 to 30 pph at 5 micron
Budit 3077	10 to 50 pph at 5 micron
Example 14 Devitrifying frit at	5 microns 100 parts
Tin at	5 to 15 pph at 5 micron
Zinc at	5 to 45 pph at 5 micron
Mica at	5 to 30 pph at 5 micron
Zinc Borate at	5 to 30 pph at 5 micron
NH-1197	10 to 50 pph at 5 micron
Example 15 Devitrifying frit at	30 microns 100 parts
Tin at	5 pph
Zinc at	10 pph
Zinc Borate at	10 pph
Sodium Pyrophosphate at	10 pph
Mica	10 pph

This mix gave a melt and flow temperature of 230°C with an intumescence starting at 450°C and ceasing at 800°C. Removing the sodium pyrophosphate gave a similar performance without the intumescence.

Example 16

Another mix, Ceepree ® M at 5 microns 100 parts together with the formula as in Example 15 gave results which were very similar. The composition was more suitable for extrusion and injection moulding because of the small particle size, although

more expensive to produce.

Example 17

As Example 16 but with the addition of 10 ppm of fine ground mica. The result was an improved electrical insulation when compounded and extruded both at room temperature and in a simulated fire.

Example 18	Devitrifying frit at	30 microns 100 parts
	Tin at	1 to 25 pph at 5 micron
	Zinc at	1 to 30 pph at 5 micron
	Mica at	30 pph at 5 micron
Example 19	Devitrifying frit at	5 microns 100 parts
	Tin at	1 to 25 pph at 5 micron
	Zinc Borate	1 to 30 pph at 5 micron
	Zinc at	1 to 45 pph at 5 micron
	Mica at	1 to 30 pph at 5 micron
Example 20	Devitrifying frit at	30 microns 100 parts
	Tin at	1 to 30 pph
	AOM (Molybdinate) at	1 to 5 pph
	Zinc at	1 to 20 pph
	Zinc Borate at	1 to 40 pph
	Sodium Pyrophosphate at	1 to 30 pph

Example 21	Devitrifying frit at	5 microns 100 parts
	Tin at	5 to 15 pph at 5 micron
	Zinc at	5 to 45 pph at 5 micron
	Mica at	5 to 30 pph at 5 micron
	Zinc Borate at	5 to 30 pph at 5 micron
	Budit 3077	10 to 50 pph at 5 micron
Example 22	Devitrifying frit at	5 microns 100 parts
	Tin at	5 to 15 pph at 5 micron
	Zinc at	5 to 45 pph at 5 micron
	Mica at	5 to 30 pph at 5 micron
	Zinc Borate at	5 to 30 pph at 5 micron
	NH-1197	10 to 50 pph at 5 micron

These blends were compounded into a range of thermoplastic materials including PVC, PVA, silicone and fluoropolymers, acrylics, EVA, PP, LDPE, PE, Nylon, EPDM and polyurethane, and thermosetting resins, such as polyester, epoxy and phenolic resins. The inclusion rate was in the 25 to 35% by weight range. There was some flaming but this was extinguished as the composite blend melted, flowed and intumesced. It was found that using a pentaerythritol ester based plasticizer, such as trade named Heroflex 707, gave a good flame and smoke suppression, particularly in PVC. Alumina trihydrate, hydrated magnesium calcium carbonate, and magnesium hydroxide can also be used as flame retardants but in significantly lower amounts than are normally specified. A Great Lakes powdered phosphate NH-1197, a general flame retardant, can be mixed with all of the above blends at a rate of 10 to 55 pph depending

on the degree of flame retardancy required as can any of the appropriate Budit range.

Boric acid coated with Dow Corning's silicone oil 1107 may be included in any of the example formulae at 5 to 100 pph.

CLAIMS

1. A fire barrier material comprising two or more frits capable of melting progressively as the temperature rises under fire conditions, one of said frits being a relatively low-melting frit and another of said frits being a relatively high melting devitrifying frit and at least one of:-
 - (a) a pH buffer;
 - (b) one or more of substances to reduce melt and flow temperature of the frits; and
 - (c) an intumescence substance.
2. A fire barrier material as claimed in claim 1 wherein the pH buffer is one that reduces the pH of the frit compositions to a low alkalinity or neutral pH.
3. A fire barrier material as claimed in claim 2 wherein the pH buffer provides a pH reduction to 8.5 or lower.
4. A fire barrier material as claimed in claim 2 or claim 3, wherein the pH buffer includes phosphates.
5. A fire barrier material as claimed in claim 4 wherein the phosphates are selected from the group consisting of sodium pyrophosphate, ammonium monophosphate and ammonium polyphosphate.
6. A fire barrier material as claimed in any one of the preceding claims wherein the substances to bring down melt and flow temperatures are a combination of substances that produce a first melt zone in the range of 220 to 270°C, a second melt zone in the range 270 to 420°C and a third melt zone in the range of 420°C upwards.

7. A fire barrier material as claimed in any one of the preceding claims wherein one of the substances to bring down melt and flow temperature of the frit compositions is zinc borate.
8. A fire barrier material as claimed in claim 7 wherein magnesium carbonate and/or zinc spar is/are added to the zinc borate to reduce the melt temperature further.
9. A fire barrier material as claimed in any one of the preceding claims wherein one or more powdered metals are included in the frit mix to reduce the melt temperature further.
10. A fire barrier material as claimed in claim 9 wherein powdered tin with a melt temperature of around 228°C is included in the material.
11. A fire barrier material as claimed in claim 10 wherein powdered zinc with a melting point of around 420°C is included as a second metal in the frit mix.
12. A fire barrier material as claimed in claim 10 or claim 11 wherein zinc borate is included in the frit mix.
13. A fire barrier material as claimed in any one of the preceding claims wherein mica is included in the material to act as a high temperature adhesive.
14. A fire barrier material as claimed in any one of the preceding claims wherein boric acid is included in the material as a glass-forming agent.
15. A fire barrier material as claimed in claim 14 wherein the boric acid is coated.
16. A fire barrier material as claimed in claim 15 wherein the boric acid is coated with a silicone oil.
17. A fire barrier material as claimed in claim 14, 15 or 16 wherein the boric acid is included in amounts from 5 to 100 pph.

18. A fire barrier material as claimed in any one of the preceding claims wherein the material is provided with a coating to improve its mechanical and electrical properties.
19. A fire barrier material as claimed in any one of the preceding claims wherein the material is provided in powder form.
20. A composition of glass frits comprising at least one devitrifying or high temperature melting frit and a powder blend to neutralise pH of the composition and to drop the melt and flow temperature.
21. A composition as claimed in claim 20 wherein the powder blend is selected from ammonium molybdate, sodium pyrophosphate, ammonium monophosphate, ammonium polyphosphate, zinc borate, zinc and tin powdered metals, melamine, pentaerythritol and melamine phosphate.
22. A composition as claimed in claim 20 or 21 further comprising at least one low melt frit.
23. A composition as claimed in claim 20, 21 or 22, wherein substances are included in the composition to reduce the melt and flow temperatures of the frits.
24. A composition as claimed in claim 23 wherein the substances are a combination of substances that produce a first melt zone in the range of 220 to 270°C, a second melt zone in the range 270 to 420°C and a third melt zone in the range of 420°C upwards.
25. A composition as claimed in claim 23 or 24 wherein one of the substances to bring down melt and flow temperature of the frit compositions is zinc borate.

26. A composition as claimed in claim 25 wherein magnesium carbonate and/or zinc spar is/are added to the zinc borate to reduce the melt temperature further.
27. A composition as claimed in any one of claims 20 to 26 wherein mica is included in the composition to act as a high temperature adhesive.
28. A composition as claimed in any one of claims 20 to 27 wherein boric acid is included in the composition as a glass-forming agent.
29. A composition as claimed in claim 28 wherein the boric acid is coated.
30. A composition as claimed in claim 29 wherein the boric acid is coated with a silicone oil.
31. A composition as claimed in any one of claims 28 to 30 wherein boric acid is included in amounts from 5 to 100 pph.
32. A composition as claimed in any one of claims 20 to 31 wherein the composition is provided with a coating to improve its mechanical and electrical properties.
33. A composition as claimed in any one of claims 20 to 32 wherein the composition is provided in powder form.
34. A fire barrier material comprising a combination of materials capable of melting progressively as the temperature rises under fire conditions, namely a relatively high melting devitrifying frit, one or more substances to reduce melt and flow temperature of the frit and optionally an intumescent substance.
35. A fire barrier material as claimed in claim 34 further comprising a pH buffer.
36. The use of a fire barrier material according to claims 1 to 19 or claims 34 and 35 in acid and/or ester cured thermosetting resins.

37. The use of a fire barrier material according to claims 1 to 19 or claims 34 and 35 in catalyst cured thermosetting resins.
38. The use of a composition according to claims 20 to 33 in acid and/or ester cured thermosetting resins.
39. The use of a composition according to claims 20 to 33 in catalyst cured thermosetting resins.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01792

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K21/02 C08K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 02545 A (ALCAN INT LTD ;WAINWRIGHT ROBIN (GB); EVANS KENNETH ARTHUR (GB)) 3 February 1994 (1994-02-03) page 13 ----- GB 2 234 754 A (CROMPTON GEOFFREY) 13 February 1991 (1991-02-13) cited in the application examples 5,9 ----- US 5 175 197 A (GESTNER ROBERT E ET AL) 29 December 1992 (1992-12-29) examples 6-8 ----- -----	1,6,7, 20-25,34 1-5, 20-23, 34,35 1-7, 20-25, 34,35 -/-
X		

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

23 August 2000

Date of mailing of the international search report

21/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentdaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01792

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 04291 A (CROMPTON DESIGN MFG) 4 April 1991 (1991-04-04) page 5, line 5 - line 22; examples 1,3 _____	1, 6, 7, 20-25, 35-39
A	WO 94 01492 A (FERODO CAERNARFON LTD ;DAVIS ROBERT JOHN (GB)) 20 January 1994 (1994-01-20) page 1 -page 2 _____	1-39
A	EP 0 349 320 A (CROMPTON DESIGN MFG) 3 January 1990 (1990-01-03) page 2, column 1, line 46 - line 55 _____	1-39
A	PARRY, DAVID J. ET AL: "Ceepree: unique fire barrier from a versatile filler" CELL. POLYM. (1990), 9(3), 195-205 , XP002145540 the whole document _____	1-39

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/01792

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9402545 A	03-02-1994	AT 148143 T AU 4579493 A CA 2140037 A DE 69307709 D DE 69307709 T DK 650507 T EP 0650507 A FI 950179 A JP 8508051 T NO 950162 A US 5532292 A	15-02-1997 14-02-1994 03-02-1994 06-03-1997 04-09-1997 28-07-1997 03-05-1995 16-01-1995 27-08-1996 16-01-1995 02-07-1996
GB 2234754 A	13-02-1991	AT 91143 T AT 140952 T AU 610867 B AU 1448588 A DE 3855459 D DE 3855459 T DE 3882070 A DE 3882070 T DK 197088 A EP 0287293 A EP 0420302 A ES 2094134 T FI 881670 A, B, GB 2203157 A, B HK 597 A JP 2772354 B JP 63273690 A NO 176054 B US 4879066 A	15-07-1993 15-08-1996 30-05-1991 13-10-1988 05-09-1996 20-02-1997 05-08-1993 28-10-1993 12-10-1988 19-10-1988 03-04-1991 16-01-1997 12-10-1988 12-10-1988 10-01-1997 02-07-1998 10-11-1988 17-10-1994 07-11-1989
US 5175197 A	29-12-1992	AU 640729 B AU 6921091 A DE 69022570 D DE 69022570 T EP 0438906 A JP 4211464 A	02-09-1993 11-07-1991 26-10-1995 02-05-1996 31-07-1991 03-08-1992
WO 9104291 A	04-04-1991	AU 631253 B AU 6404090 A CA 2060317 A EP 0491798 A JP 5500676 T NO 915126 A	19-11-1992 18-04-1991 15-03-1991 01-07-1992 12-02-1993 27-12-1991
WO 9401492 A	20-01-1994	GB 2268497 A, B	12-01-1994
EP 0349320 A	03-01-1990	AU 617193 B AU 3722989 A DK 327989 A FI 893193 A GB 2220208 A, B JP 2209947 A NO 892711 A US 5053077 A ZA 8904993 A	21-11-1991 04-01-1990 31-12-1989 31-12-1989 04-01-1990 21-08-1990 02-01-1990 01-10-1991 26-09-1990